Cyclobutane — physical properties and theoretical studies

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I. INTRODUCTION

Cyclobutane is interesting because it provides a bridge between the very reactive (for a hydrocarbon) cyclopropane and the 'normal' cycloalkanes from cyclopentane to the larger cycloalkanes. Cyclopropane reacts readily with bromine to form 1,3-dibromopropane[1] and reacts with sulfuric acid to give 1-propylsulfuric acid[2]. Cyclobutane does not react with either of these reagents, but some cyclobutanes undergo C−C bond cleavage with transition metal species[3]. It is very difficult to cleave the C−C bonds of cyclopentane and the higher cycloalkanes.

II. CYCLOALKANE STRUCTURES AND BONDING

In order to understand these differences, it is helpful to examine the structures and energies of these compounds. Some data are given in Table 1. Cyclopentane undergoes

TABLE 1.   Structural data for some cycloalkanes

Compound	Observed			Calculated		
	r(C−C)	r(C−H)	H−C−H	r(C−C)	r(C−H)	H−C−H
Cyclopropane [a]	1.512(3)	1.083(3)	114.0(7)	1.509	1.083	115.1
Cyclobutane [b]	1.556(1)	1.091(1)		1.552	1.094 ax	109.3
					1.093 eq	
Cyclopentane [c]	1.546(1)	1.114		1.540	1.095	
Cyclohexane [d]	1.536(1)	1.097(2) ax		1.530	1.099 ax	106.9
		1.085(6) eq			1.096 eq	
Cyclopropene [e]	1.505(1)	1.085(1)		1.513	1.089	114.5
	1.293(1)	1.072(1)		1.304	1.077	
Cyclobutene [f]	1.566(3)	1.094(5)		1.568	1.094	109.2
	1.517(3)			1.517		
	1.342(4)	1.083(5)		1.351	1.086	

[a] Reference 5.
[b] Reference 6.
[c] Reference 4.
[d] Reference 9.
[e] R. J. Berry and M. D. Harmony, *Struct. Chem.*, **1**, 49 (1990).
[f] B. Bak, J. J. Led, L. Nygaard, J. Rastrup-Andersen and G. O. Sørensen, *J. Mol. Struct.*, **3**, 369 (1969).

pseudorotation in which the carbons undergo a motion perpendicular to the average plane without significant change in energy[4]. The average C−C bond length is only 0.013 Å greater than that of *n*-alkanes. In contrast, cyclopropane has markedly shorter C−C bond lengths[5] and cyclobutane has markedly longer C−C bond lengths[6].

The short bond lengths in cyclopropane are in part explained using the Coulson–Moffitt bonding model[7]. With nominal 60° C−C−C bond angles, it is not possible to form coaxial C−C bonds since the smallest interorbital angle for first row elements is 90°, corresponding to pure *p*-orbitals. The angle must be somewhat larger since a bond formed with just *p*-orbitals will be quite weak. They estimated an interorbital angle of 104°, corresponding to 80% *p*-character in the C−C bonds vs. the normal value of about 75% *p*-character. Thus, the bonds in cyclopropane are bent, and a better representation of the bond length would be given by the path of maximum electron density between the carbons (the bond path)[8] and it has been estimated to be 1.528 Å. It is approximately 0.008 Å shorter than the C−C bonds in cyclohexane[9].

The bent bonds in cyclopropane derivatives are readily observed in the results of X-ray crystallographic studies[10]. The output of such a study is an electron density map, and the maximum in electron density between two cyclopropane carbons lies outside the line of centers of the atoms. Bond angle bending based on *ab initio* calculations may be described in terms of the angle between the C−C bond paths at the C nucleus. With cyclopropane, the angle deviates from the conventional angle by 18.8° whereas the deviation for cyclobutane is only 6.7°[11].

The structure of cyclobutane presents some interesting questions. The C−C−C bond angle is 88°, indicating that it adopts a puckered structure[6]. This is probably due to a torsional interaction between two adjacent methylene groups. Ethane is known to prefer a staggered arrangement and the eclipsed arrangement is 3 kcal mol^{-1} higher in energy[12]. Planar cyclobutane, with a 90° C−C−C bond angle, has eclipsed methylene groups, resulting in considerable torsional strain. Puckering the ring leads to a reduction of this strain term, but at the same time the C−C−C bond angle is reduced, leading to increased bond angle strain. The equilibrium geometry is a result of the tension between these two

strain terms. The C−C−C bond angle (α) is related to the ring puckering angle (τ) by $\tan(\alpha/2) = \cos(\tau/2)$.

$$180\text{-}\tau$$

Another feature of the cyclobutane geometry is that the methylene groups are rotated inwards[13], whereas one might expect them to rotate outwards in order to reduce H$\cdots$H non-bonded interactions. Bartell and Anderson have proposed that the methylene groups prefer a local C_{2v} geometry, and with bent C−C bonds this would result in the inward bend.

The most puzzling feature of the cyclobutane geometry is the long C−C bond length. This has been observed in a variety of cyclobutane derivatives, and C−C bond lengths cover a range of 1.521–1.606 Å depending on the substitution pattern, with an average of 1.554 Å[14]. With cyclobutane itself, the bond length is 1.556 Å[6].

The short C−C bond length in cyclopropane and the long length in cyclobutane may be explained by invoking a 1−3 C$\cdots$C non-bonded repulsion[15]. It might be noted that this is contained in the Urey–Bradley force field[16]. Cyclopropane does not have such an interaction because all of the carbons are bonded to each other. Cyclobutane, on the other hand, has two 1−3 C$\cdots$C non-bonded interactions with a relative small distance between the carbons. This repulsion will lead to a lengthening of the C−C bonds.

One might wonder if it would also lead to flattening of the ring in order to minimize this interaction. An *ab initio* calculation for cyclobutane gives a bond length of 1.555 Å and a CCC bond angle of 88°. If the C−C length is forced to be 1.536 Å (the cyclohexane bond length) and the geometry is again optimized, the CCC bond angle changes very little and the energy increases by only 0.4 kcal mol^{-1} [17]. Near their equilibrium values, bonds can initially be stretched with little increase in energy, but further extension become costly because of the quadratic nature of the bond stretching potential.

This proposal also explains why cyclopentane has C−C bonds a little longer than those in cyclohexane. The 1,3-C$\cdots$C non-bonded distances are shorter in cyclopentane than in cyclohexane[18], leading to greater repulsion in the former. It also explains the observed 111° C−C−C bond angles in *n*-alkanes.

III. BOND STRENGTHS

The high *p*-character in the C−C bonds of cyclopropane must lead to high *s*-character in its C−H bonds. It is known that increasing *s*-character leads to shorter and stronger C−H bonds[19], and this is found with cyclopropane (Table 2). The force constant for stretching the C−H bond is significantly greater than for cyclobutane, the bond length is shorter, and the bond dissociation energy is greater than found with other cycloalkanes or open chain alkanes. The effect is further increased with cyclopropene. Here, the olefinic C−H bond would have an *s*-character approaching that of acetylene, and it is one of the few unsubstituted hydrocarbons that will undergo base catalyzed exchange of the vinylic C−H bonds with ROD to give C−D bonds[20].

The properties of the C−H bonds in cyclobutane are much closer to those of the other cycloalkanes, although there is an indication of somewhat increased *s*-character. The C−H bond lengths are somewhat shortened, and the bond dissociation energy is calculated to be 1.5 kcal mol^{-1} greater than in cyclohexane. Further information may be gained from the ^{13}C−H NMR coupling constants (see below).

TABLE 2.   Cycloalkane C−H force constants
and bond dissociation energies

Compound	k(C−H)[a]	BDE[b]
Cyclopropane	6.3	108.4
Cyclobutane	5.1[c]	99.8[c]
Cyclopentane	4.2[c]	95.5[c]
Cyclohexane	5.3[c]	98.4[c]

[a] Calculated at the B3LYP/6-311+G* level of theory.
[b] In kcal mol^{-1}; calculated at the G3B3 level of theory[17].
[c] Equatorial hydrogens.

IV. ENERGIES OF CYCLOALKANES

The heats of formation of a number of small cycloalkanes and related compounds have been determined via combustion calorimetry, and additional data have been obtained by measuring heats of hydrogenation. Some representative data are summarized in Table 3.

One item of interest with these compounds is the strain energy. This is defined as the difference in heat of formation between the compound of interest and that of an 'unstrained model'. The choice of this model has been the subject of some controversy, but almost any choice would be satisfactory as long as it is applied consistently. The values of the strain energies may differ, but the only quantities of importance are the relative values. The Franklin group equivalents[21] (Table 4) are frequently used for this purpose.

TABLE 3.   Heats of formation and strain energies of cycloalkanes, gas phase, 25 °C, kcal mol^{-1}

Compound	ΔH_f	Strain energy	Reference
Cyclopropane	12.7 ± 0.1	27.5	a
Cyclobutane	6.6 ± 0.3	26.3	b
Cyclopentane	−18.3 ± 0.2	6.3	b
Cyclohexane	−29.5 ± 0.2	0.0	b
Cyclopropene	66.2 ± 0.6	52.2	c
Cyclobutene	37.4 ± 0.4	28.4	d
Cyclopentene	8.1 ± 0.3	4.0	e
Cyclohexene	−1.2 ± 0.1	0.4	f
1-Methylcyclopropene	58.6 ± 0.3	53.5	d
Methylenecyclopropane	29.1 ± 0.2	32.7	d
Bicyclo[1.1.0]butane	51.9 ± 0.2	63.9	d
Bicyclo[2.1.0]pentane	37.8 ± 0.3	54.8	g
Bicyclo[2.2.0]hexane	29.8 ± 0.3	51.7	g
Bicyclo[1.1.1]pentane	50.4	71.0	h
Cubane	148.7 ± 0.9	157.4	i
Bis(1,1′-bicyclo[1.1.1] pentane)	96.8 ± 1.2	126.9	j

[a] J. W. Knowlton and F. D. Rossini, *J. Res. Natl. Bur. Stand.*, **43**, 113 (1949).
[b] S. Kaarsaemaker and J. Coops, *Recl. Trav. Chim. Pays-Bas*, **71**, 261 (1952).
[c] K. B. Wiberg, W. J. Bartley and F. D. Lossing, *J. Am. Chem. Soc.*, **84**, 3980 (1962).
[d] K. B. Wiberg and R. A. Fenoglio, *J. Am. Chem. Soc.*, **90**, 3395 (1968).
[e] M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky and W. E. Vaughan, *J. Am. Chem. Soc.*, **59**, 831 (1937).
[f] A. Labbauf and F. D. Rossini, *J. Phys. Chem.*, **65**, 476 (1961).
[g] W. R. Roth, F.-G. Klärner and H.-W. Lennartz, *Chem. Ber.*, **113**, 1818 (1980).
[h] Calculated energy: K. B. Wiberg, *J. Comput. Chem.*, **5**, 197 (1984).
[i] B. D. Kybett, S. Carroll, P. Natalis, D. W. Bonnell, J. L. Margrave and J. L. Franklin, *J. Am. Chem. Soc.*, **88**, 626 (1966). However, see V. V. Diky, M. Frenkel and L. S. Karpushenkava, *Thermochim. Acta* **408**, 115 (2003).
[j] V. A. Luk'yanova, V. P. Kolesov and V. P. Vorob'eva, *Russ. J. Phys. Chem.* (*Engl. Transl.*), **69**, 1908 (1995).

TABLE 4. Franklin's group equivalents, ΔH_f kcal mol^{-1} (25 °C) [a]

Group	Value
CH$_3$	−10.12
CH$_2$	−4.926
CH	−1.09
C	0.80
=CH$_2$	6.25
cis-CH=CH	18.88
C=CH	20.19

[a] Reference 21.

The strain energy of cyclobutane is then the heat of formation of cyclobutane less four times the CH$_2$ equivalent, or 26 kcal mol^{-1}. The strain energies of some compounds of interest are given in Table 3. Cyclohexane has essentially no strain energy; cyclopentane has a small strain energy which results from the partial eclipsing of adjacent C−H bonds plus some bond angle strain. Cyclopropane and cyclobutane have essentially the same strain energy, which at first appears surprising in view of the large difference in C−C−C bond angles, and the difference in hybridization. One factor that may contribute to the strain energy of cyclobutane is the cross-ring 1−3 repulsion between the methylene carbons[15]. This is not present in cyclopropane.

There is another important factor that contributes to the lack of difference in strain energies. The C−H bonds in cyclopropane are considerably stronger than those in cyclobutane. If the normal C−H bond dissociation energy (cyclohexane) is 98 kcal mol^{-1}, a C−H bond in cyclopropane is 10 kcal mol^{-1} stronger. With six C−H bonds, this could lead to a net stabilization that may approach 60 kcal mol^{-1}. The strain in the carbon skeleton of cyclopropane may approach 88 kcal mol^{-1}, and for cyclobutane, with 8 C−H bonds that are 1.5 kcal mol^{-1} stronger than those in cyclohexane, the strain may approach 38 kcal mol^{-1}. This is, of course, only a very rough approximation, but it does indicate that the strain in the skeleton of cyclopropane is significantly greater than that for cyclobutane, and that for the latter is still considerable.

The heats of hydrogenation of cyclopropene, methylenecyclopropane and cyclobutene are interesting. The heat of hydrogenation of cyclohexene (assumed to be unstrained) is just the difference in heat of formation between cyclohexene and cyclohexane, or 28 kcal mol^{-1}. Cyclobutene has a heat of hydrogenation of 31 kcal mol^{-1}, only a little larger than for cyclohexene, indicating that the introduction of a C=C bond does not lead to much of an increase in strain energy.

The value for cyclopentene is 26 kcal mol^{-1}, indicating that cyclopentene is less strained than cyclopentane because some of the methylene eclipsing strain in cyclopentane is relieved on going to cyclopentene.

Cyclopropene is remarkable, giving a heat of hydrogenation of 54 kcal mol^{-1}, 26 kcal mol^{-1} greater than that for cyclohexene. This effect is reduced somewhat in methylenecyclopropane and can be seen by comparing its heat of formation with the isomeric 1-methylcyclopropene. The origin of the high heat of hydrogenation has been attributed to the strong C−H bonds in cyclopropane that are lost on going to cyclopropene[22]. The effect is smaller with methylenecyclopropane since it has only one trigonal center in the ring.

V. NMR SPECTRA OF CYCLOALKANES

There are interesting differences between the NMR chemical shifts of cyclopropane, cyclobutane and the higher cycloalkanes (Table 5). The ^{1}H shift for cyclopropane is

TABLE 5.   NMR chemical shifts (ppm) [a]

Compound	^{1}H		^{13}C	
	CH$_2$	=CH	CH$_2$	=CH
Cyclopropane	0.22		−2.6	
Cyclobutane	1.96		23.3	
Cyclopentane	1.51		26.5	
Cyclohexane	1.54		27.8	
Cyclopropene	0.93	7.06	2.3	108.9
Cyclobutene	2.57	6.03	31.4	137.2
Cyclopentene	2.28 [b]	5.60	32.3 [c], 22.7	130.2
Cyclohexene	1.96 [b]	5.59	25.1 [c], 22.6	126.9

[a] Reference 28.
[b] Protons adjacent to the double bond.
[c] Methylene carbons adjacent to the double bond.

TABLE 6.   NMR ^{13}C−H coupling constants [a]

Compound	J ^{13}C−H (Hz)	%s
Methane	125	25
Cyclopropane	161	32
Cyclobutane	134	27
Cyclohexane	123	25
Bicyclo[1.1.0]butane	153 (equatorial)	31
	169 (axial)	34
	205 (bridgehead)	41
Bicyclo[1.1.1]pentane	144 (methylene)	29
	164 (bridgehead)	33
Cubane	154	31
Cyclopropene [b]	228.2	46
Cyclobutene [b]	170	34
Cyclopentene [b]	162	32
Cyclohexene [b]	158	31

[a] Data were taken from Reference 28.
[b] Vinylic hydrogens.

found to be remarkably upfield, and this has been used as a diagnostic for the presence of a cyclopropane ring[23]. Cyclobutane, on the other hand, has its ^{1}H band downfield from that in cyclohexane. The same trend is found with the ^{13}C shifts.

The upfield shift for cyclopropane has been attributed to a ring current associated with σ-aromaticity, and the downfield shift for the cyclobutane protons has been attributed to σ-antiaromaticity. The subject of σ-aromaticity has been the object of many studies. Recent work suggests that it is not a viable proposal[24]. Nevertheless, it is clear that cyclopropane has a higher than normal magnetic susceptibility[25]. In addition, the nucleus independent chemical shifts (NICS) at the center of the ring for cyclopropane is positive[26] and that for cyclobutane is negative[26, 27]. This quantity has been suggested as a test for aromaticity and antiaromaticity respectively, although the detailed origin of these shifts is not as yet understood.

The ^{13}C−H NMR coupling constants can be used to gain information on hybridization[28] and the empirical relationship %s = J ^{13}C−H/5 has been proposed. The values of these coupling constants are given in Table 6 for cyclobutane and a number of other related

compounds, along with the empirically derived %s values. Again, the cyclobutane C−H bonds appear to have increased s character, but not as much as is found with cyclopropane.

Large long-range ^{1}H−^{1}H coupling constants are observed with cyclobutyl derivatives. One of the largest, 18 Hz, is found for the bridgehead hydrogens of bicyclo[1.1.1]pentane (**1**)[29]. With bicyclo[2.1.1]hexane (**2**), there is a 6 Hz coupling between the *endo* protons of the cyclobutane methylene groups[30]. When the distance is further increased as in bicyclo[2.2.1]heptane (**3**), the coupling between the bridgehead hydrogens is less than 1 Hz[31]. The coupling presumably involves the overlap of the backsides of the C−H bond orbitals which increases rapidly as the distance is decreased.

(**1**)   (**2**)   (**3**)
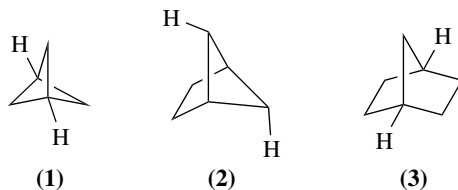
## VI. CYCLOPROPYL AND CYCLOBUTYL CATIONS

In contrast to most reactions in which cyclopropane derivatives are more reactive than cyclobutanes, the opposite is true for solvolytic reactions. Cyclopropyl tosylate is relatively unreactive[32], and its lack of reactivity has been attributed to two factors. First, an S_N1 solvolytic reaction would normally lead to an increase in C−C−C bond angle at the reaction site as a carbocation is formed, and this is not possible with a cyclopropane ring[33]. As a result, there is an increase in strain energy. Second, the hybridization of the carbons in cyclopropane is close to that of ethylene, and vinyl halides are resistant to solvolytic reactions[34]. Despite its low reactivity, it is important to note that it is considerably more reactive than 7-norbornyl tosylate that has a 94° C−C−C bond angle[35]. It appears that the solvolysis of cyclopropyl tosylate is assisted by the development of allyl cation character in the transition state[36].

Cyclobutyl tosylate (**4**) would be expected to have reduced reactivity because it, again, will suffer an increase in strain on going to a carbocation due to the constrained C−C−C bond angles. However, it has a reactivity comparable to cyclopentyl tosylate[35b]. There is now much evidence that cyclobutyl cations are stabilized by an interaction with the cross-ring carbon, leading to a species that might be described as a 'bicyclobutonium ion' (**5**)[37] in which the cationic center is stabilized by an interaction with the cross-ring methylene group.

(**4**)   (**5**)
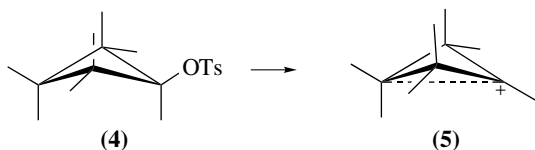
The cross-ring distance is important for such an interaction, and it increases in importance as the distance is decreased. Thus, 1-chlorobicyclo[1.1.1]pentane (**6**) is quite reactive[38].

5-Substituted bicyclo[2.1.1]hexane derivatives are interesting in that the *endo*-tosylate (**7**) is 10^6 times as reactive in solvolysis as the *exo*-tosylate (**8**)[39]. This indicates the need

(6)

(7)   **(8)**
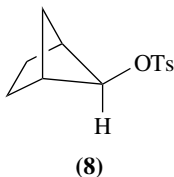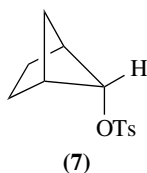
for the remote carbon of the cyclobutane ring to be *anti* to the leaving group in order to have an assisted solvolysis. This appears to be a general feature of the solvolysis of bridged cyclobutyl derivatives[40].

In these solvolytic reactions, cyclopropylcarbinyl and cyclobutyl cations frequently are interconverted. B3LYP/6-311+G* calculations for the parent ions find both to be minima on the potential energy surface, with the cyclobutyl cation slightly lower in energy (1 kcal mol^{-1}). These ions are in rapid equilibrium, and substitution can easily shift the equilibrium composition[41].

VII. INTERACTION OF CYCLOPROPANE AND CYCLOBUTANE RINGS WITH ELECTRON-DEFICIENT CENTERS

The interaction of cyclopropane rings with a cationic site has been well studied. With dimethylcyclopropylcarbinyl cation, the 'bisected' conformer, in which the cationic *p*-orbital is aligned to interact with the bent C−C bonds of the cyclopropane ring, has a 14 kcal mol^{-1} lower energy than the 'perpendicular' conformer, with the latter being a transition state[42]. The ion can be observed by NMR spectroscopy. Methyl substitution at the cationic center is important since cyclopropylcarbinyl cation rearranges to a bridged cyclobutyl cation[38]. The interaction of the cyclopropane ring with an electron-deficient center is also seen with cyclopropylcarboxaldehyde where the rotational barrier is 6 kcal mol^{-1} [43]. The minimum energy conformers correspond to the 'bisected' arrangement and the transition state has the 'perpendicular' arrangement.

The interaction with a cationic site is much weaker with cyclobutane. The rotational barrier for cyclobutanecarboxaldehyde has not been measured, but calculations indicate it is only 0.8 kcal mol^{-1} [44]. There are two low energy conformers where the carbonyl group is eclipsed with either the adjacent hydrogen or one of the adjacent carbons. A rotamer corresponding to the perpendicular conformer is neither a minimum nor a transition state.

Dimethylcyclobutylcarbinyl derivatives (**9**) on solvolysis rearrange to cyclopentyl cations. Relief of strain energy is an important driving force, but this is reduced by the conversion of a tertiary cation to the usually less stable secondary cation[45]. In order to stabilize a cyclobutylcarbinyl cation enough to allow it to be observed by NMR, it was necessary to have two cyclopropane rings attached to the cationic center[46].

(9)
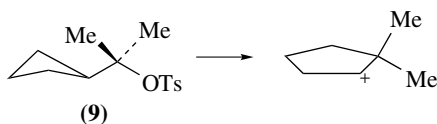
VIII. PROTONATED CYCLOPROPANES AND CYCLOBUTANES

As noted in the introduction, cyclopropanes are readily cleaved by electrophiles whereas this is not true with cyclobutanes. The reason is not thermodynamic since the overall heats of reaction are essentially the same. The proton affinity of cyclopropane has been measured and is 179 kcal mol^{-1} [47]. With cyclopropane, the interaction with protons is known to give a protonated cyclopropane intermediate[48]. The proton affinity of cyclobutane does not appear to have been measured, but B3LYP/6-311+G* calculations indicate its proton affinity to be about 10 kcal mol^{-1} lower than for cyclopropane. This is easily seen in the energies of transferring a proton from isopropyl cation to cyclopropane and cyclobutane:

$$\Delta H = 2.3 \text{ (calc)}$$
$$\Delta H = 1.0 \text{ (obs)}$$

$$\Delta H = 13.4 \text{ (calc)}$$
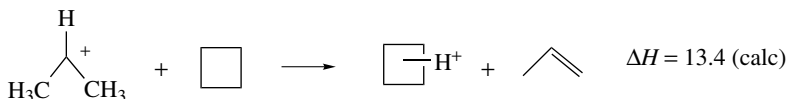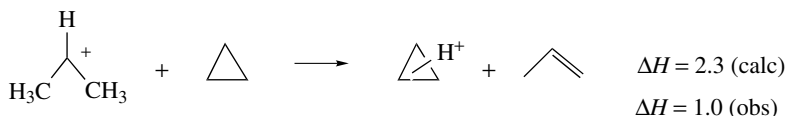
The difference between these compounds has been studied by theoretical calculations. The protonation of cyclopropane may occur at either a corner or an edge, and experimental evidence suggests that both have comparable energies and can easily be interconverted. The structures of the two ions are shown in Figure 1, and are compared with the corresponding ions derived from cyclobutane[49]. Corner protonated cyclopropane is calculated to be the ground state, with the edge protonated ion being a transition state 4 kcal mol^{-1} higher in energy[17]. Edge protonated cyclobutane is calculated to be the ground state, with the corner protonated ion being a transition state 12 kcal mol^{-1} higher in energy.

Corner protonated cyclopropane is essentially a methyl cation coordinated with ethylene, whereas corner protonated cyclobutane appears like a methyl cation coordinated with a trimethylene diyl. Not surprisingly, the former has the lower energy. With the edge protonated ions, the proton in the C3 ion is able to achieve bonding with the strongly bent cyclopropane bonds thus remaining farther away from the carbons and not perturbing the geometry as much as is found with the C4 ion. Again, it is not surprising that the edge protonated cyclopropane has a lower energy than the edge protonated cyclobutane.

It should be noted that three- and four-membered rings may also be cleaved by nucleophiles with three-membered rings being more reactive than four-membered rings[50]. Here again, the overall change in energy is about the same for cyclopropane and cyclobutane, and the more facile cleavage of cyclopropanes must be due to an additional factor.

IX. THERMAL FORMATION OF CYCLOBUTANES BY CYCLOADDITION AND THERMAL CLEAVAGE

Cycloaddition of alkenes to form cyclobutanes normally does not occur thermally because at temperatures at which the reaction might occur the free energy of reaction is positive. This is a result of the unfavorable entropy effect that results from two molecules combining to form one. It can be overcome if the two C=C bonds are in the same molecule (**10**), and here the cyclobutane ring is formed on heating[51]. It is interesting to note that the free energy of cyclobutane at 25 °C is lower than that of two ethylenes, and if a suitable catalyst could be found, cyclobutane could be formed by the dimerization of ethylene.
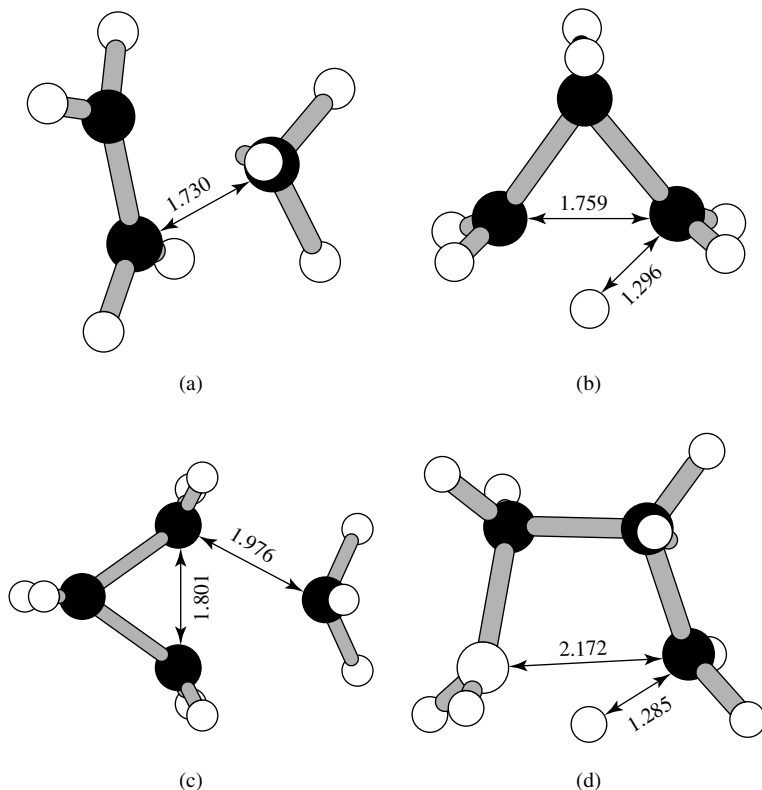
FIGURE 1. (a) Corner protonated cyclopropane, (b) edge protonated cyclopropane, (c) corner protonated cyclobutane and (d) edge protonated cyclobutane. The ground state structures are (a) and (d), whereas (b) and (c) are transition states. The structures are derived from B3LYP/6-311++G** calculations

However, because of the negative entropy of dimerization, as the temperature is raised the free energy become less negative, and then positive at temperatures where cyclobutane is converted to ethylene.


(10)
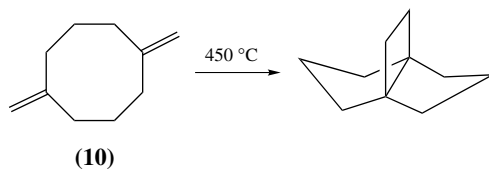
This type of reaction can also occur if the double bond is sufficiently destabilized. As an example, bicyclo[2.2.0]hex(1,4)ene (**11**) undergoes dimerization at room temperature in dilute solution leading to a propellane (**12**) that undergoes cleavage to a diene (**13**). If the reaction is carried out using higher concentrations, the main product is a polymer.

This is in accord with the initial combination of two molecules of the alkene to form a diyl. When the concentration is low, closure to the propellane predominates, but if the concentration is higher, the diyl can react with another diene to start polymerization.

(11)   **(12)**   **(13)**
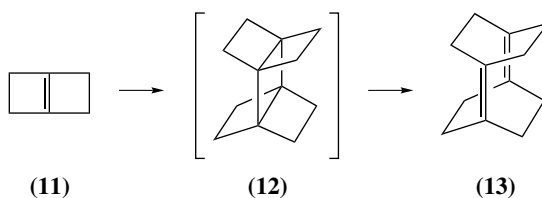
The dimerization leading to a cyclobutane is best studied by examining the reverse process, the thermal cleavage of cyclobutanes. There is now good evidence that the reaction proceeds via the initial formation of a 1,4-diyl which then is cleaved to give two alkenes[52]. Thus, the thermolysis of cyclobutanes is initially very similar to the thermal cleavage of cyclopropanes[53], except that it occurs at higher temperatures.

The thermolysis of propellanes that contain a cyclobutane ring has received some study. There is a remarkable difference in the rates of reaction of the isomeric [3.2.1]propellane (**14**)[51] and [2.2.2]propellane (**15**)[54]. The former is quite unreactive whereas the known derivative of the latter undergoes cleavage at room temperature. One factor is the difference in strain energy, with the latter having the higher strain energy because it contains three small rings.

(14)

(15)
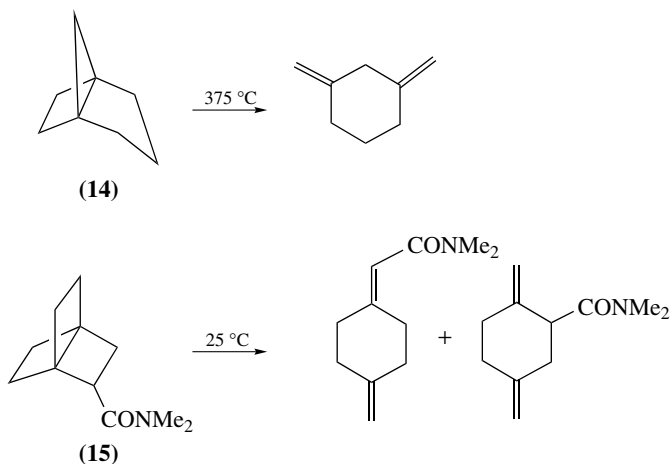
An examination of a series of [*n*.2.1]propellanes indicated that the rates of thermolysis are related to the relief of strain on going to a 1,4-diyl. However, there is possibly an additional factor that leads to the reactivity of [2.2.2]propellane. Stohrer and Hoffmann[55] have suggested that when the central propellane bond can be considerably extended as a result of the relative flexibility of the rings, the ground state will have an anti-symmetric combination of orbitals at the central carbons, and this could lead to an orbital symmetry allowed ring cleavage that would facilitate reaction. A related situation is found in the thermolysis of bicyclo[2.2.0]hexane[56].

It is interesting to note that the thermal reactivity of [2.2.2]propellanes is markedly reduced when the hydrogens are replaced by fluorines[57]. Fluorine substitution on a hydrocarbon can lead to either stabilization or destabilization, and with cyclobutane stabilization is found[58].

In contrast to the normal orbital symmetry forbidden ring opening of cyclobutanes, the thermal cleavage of cyclobutenes to butadienes occurs readily via a stereocontrolled reaction which provided one of the original pieces of evidence for orbital symmetry control[59].

The addition of ketenes to alkenes is a more facile process that occurs under relatively mild conditions. It has proven to be a useful method for the synthesis of cyclobutanones[60]. The mechanism of the reaction has received extensive study. A $[2\pi_s + (2\pi_s + 2\pi_s)]$ orbital symmetry allowed process has been proposed to account for the ease of reaction[61]. A recent study suggests that the reaction is relatively complex[62].

X. ANTIAROMATICITY IN CYCLOBUTADIENE

In 1967 Breslow and coworkers found that 1,2-diphenyl-3-benzoylcyclopropene undergoes base catalyzed H/D exchange at a slower rate than the corresponding cyclopropane by a factor of 6000[63]. This led to the proposal that the 4 π-electron cyclopropenyl anion is antiaromatic, i.e. it has an energy higher than that expected if it were simply non-aromatic[64]. This has been proposed to be a general feature of conjugated cyclic systems with 4n π-electrons[27].

Cyclobutadiene (**16**) is a 4n π-electron system, and thus potentially antiaromatic[65]. It has been a synthetic goal for many years, and it was finally observed via the photolysis of α-pyrone (**17**) in an argon matrix at 10 K[66, 67]. It was found to be very reactive, and in the absence of other reagents it dimerizes to give the *syn* diene, **18**.

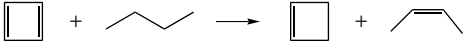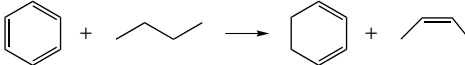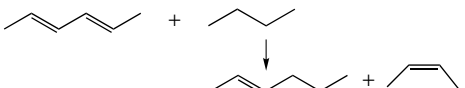(17)   (16)

(18)
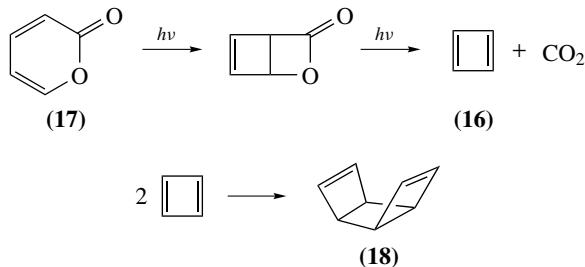
Subsequently, an iron carbonyl complex of cyclobutadiene was isolated and found to be stable at room temperature[68]. The diene could be regenerated by treatment with an oxidant, and if another compound were present, cycloaddition reactions could occur.

It has been possible to obtain an estimate of the heat of formation of cyclobutadiene via photoacoustic calorimetry[69]. This, along with theoretical estimates of its energy, allows the energy of the hydrogen transfer reaction to be calculated (Table 7). The enthalpy term for cyclobutadiene is large and negative, whereas with an aromatic compound such as benzene it is positive. A non-aromatic compound such as 2,4-hexadiene gives a small heat of reaction. The enthalpy change for the above reaction provides an estimate of the antiaromaticity of cyclobutadiene.

It is interesting to note that bicyclo[2.1.0]pent-2-ene has a heat of hydrogenation of 43 kcal mol^{-1} which is 10 kcal mol^{-1} larger than that for cyclobutene. This suggests that some antiaromatic character remains when one of the double bonds of cyclobutadiene is replaced by a cyclopropane ring[70].

TABLE 7. ΔH_f of several isodesmic reactions, kcal mol^{-1}

	ΔH	
	obs^a	calc^b
	-41 ± 11	-34.4
	33.0 ± 0.4	34.4
	4.3 ± 0.6	5.3

^{a} J. B. Pedley, *Thermochemical Data and Structures of Organic Compounds*, Thermodynamics Research Center, College Station, Texas, 1994. Hexenes: W. Fang and D. W. Rogers, *J. Org. Chem.*, **57**, 2294 (1992) and K. B. Wiberg and D. J. Wasserman, *J. Am. Chem. Soc.*, **103**, 6563 (1981).
^{b} Derived from G2 energies, Reference 27.

Antiaromatic character is a major factor only with $4n$ systems such as cyclobutadiene, cyclopropentyl anion and cyclopentadienyl cation. The energetic effect decreases rapidly with increasing ring size[63]. A recent study of the origin of antiaromaticity concluded that the antisymmetry principle is a 'hidden variable' in the π-electron calculations and that it is responsible for the destabilization of the $4n\pi$-electron systems[71].

XI. SUMMARY

Cyclobutanes have a hybridization between that of cyclopropane and cyclopentane, and is closer to the latter. This is shown by the ^{13}C−H NMR coupling constants, the C−H bond lengths and the bond dissociation energies. Cyclobutanes are unique in that they can be formed from and be cleaved into two carbon species, and both orbital symmetry forbidden and allowed processes may occur. Cyclobutanes interact with electrophiles and electron deficient centers to a greater extent than cyclopentane, but to a much smaller degree than found with cyclopropanes.

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